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Naval Ammunition Depot
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13. ABSTRACT

In an effort to predict improvements in the light output of magnesium-sodium nitrate-binder flare systems and to predict the success of other fuel-oxidizer flare systems, a semi-quantitative model is derived which relates the intensity of visible light emission from a flare to various thermodynamic properties of the combustion reactions which occur. After taking into account various energy losses, the amount of light emitted is determined.

Calculations are done using sodium nitrate and sodium perchlorate as oxidizers and various metals, e.g., aluminum, magnesium, beryllium, and silicon as fuels.

Recommendations for better illuminating flare compositions based on the thermodynamic calculations are presented. The calculations indicate that the largest realistic increase attainable for the present magnesium-sodium nitrate flare system is 2 to 3 times the present output. A 16 fold increase potential (maximum) is predicted for the aluminum-sodium perchlorate flare formula.

THEORETICAL LIGHT YIELDS FROM DIFFERENT ILLUMINATING FLARE COMPOSITIONS

SUMMARY

In an effort to predict improvements in the light output of magnesium-sodium nitrate-binder flare systems and to predict the success of other fuel-oxidizer flare systems, a semi-quantitative model is derived which relates the intensity of visible light emission from a flare to various thermodynamic properties of the combustion reactions which occur. After taking into account various energy losses, the amount of light emitted is determined.

Calculations are done using sodium nitrate and sodium perchlorate as oxidizers and various metals, e.g., aluminum, magnesium, beryllium, and silicon as fuels.

Recommendations for better illuminating flare compositions based on the thermodynamic calculations are presented. The calculations indicate that the largest realistic increase attainable for the present magnesium-sodium nitrate flare systems is 2 to 3 times the present output. A 16 fold increase potential (maximum) is predicted for the aluminum-sodium perchlorate flare formula.

OBJECTIVE

The purpose of this study is to investigate the theoretical light outputs from typical illuminating flare compositions. A semi-quantitative model for light emission will be developed which is based only on the thermodynamic properties of the combustion reactions which occur. Different methods of improving current illuminating flares will be discussed.

CONCLUSIONS AND RECOMMENDATIONS

The calculations indicate that the largest realistic increase attainable for the present magnesium-sodium nitrate flare system is 2 to 3 times the present output.

The results of other calculations indicate that for a metal fuel/sodium-containing oxidizer flare, the system which has a potential for better than an order of magnitude increase is beryllium-sodium perchlorate. Aluminum-sodium nitrate flares show a factor of five potential increase over present systems.

The magnesium-sodium perchlorate system is a feasible system. The aluminum-containing systems would be feasible if aluminum could be made to burn efficiently. The beryllium systems, while providing the highest light output, are probably too dangerous and expensive to warrant further consideration.

The following recommendations for illuminating flare studies can be made:

1. A study of magnesium-sodium nitrate flares versus magnesium-sodium perchlorate flares should be undertaken in an effort to determine if the calculations presented have any validity.

2. An investigation of the aluminum burning process should be undertaken. Various methods of alloying the aluminum or mixing it with other chemicals to facilitate burning should be studied.

3. A search should begin for less conventional systems which release large amounts of energy and have high flame temperatures. These systems do not necessarily have to contain emitters. The flames could be seeded with species which are easy to excite and emit visible light readily.

4. Chemiluminescent flame reactions in which atoms and molecules are formed directly in excited states which then emit should be investigated.

5. Extensive studies should begin on flame seeding to enhance the emission in the visible region of the spectrum.

Gains of at least 10 times the output of the present magnesium-sodium nitrate flare should be possible if methods could be developed for converting all of the energy into visible light by the processes suggested above.

INTRODUCTION AND HISTORICAL BACKGROUND

There seems to be little need to discuss the historical development of the current illuminating flare composition. An excellent review of the subject has been given by Ellern in "Military and Civilian Pyrotechnics".[1] The current illuminating flare composition consists of magnesium, sodium nitrate and an epoxy binder. This composition is used in both illuminating projectiles and air-deployed parachute flares. Typical output characteristics are a burning rate of about .09 in/sec and an efficiency of approximately 50,000 cd sec/g. A large fraction of the light emitted in the visible wavelength region is due to broadened sodium emission[2] centered at 590 nm. The detailed mechanism for excitation of sodium is not known but the excitation is more than likely thermal.[3] There is also an underlying graybody continuum and molecular emission from MgO and other reaction products. More than 75 percent of the energy liberated by the chemical reactions taking place in the combustion process is lost by convection, conduction, or radiation outside the visible.[3]

Increased light output could be obtained by using systems which liberate more energy than magnesium-sodium nitrate, systems which have a higher flame temperature and thus excite more sodium, or by systems which make more efficient use of the energy liberated by the combustion reactions.

DISCUSSION

Computation of Disposable Energy

The model chosen for this discussion is based on thermal excitation of atomic species. In this model we will calculate the energy released by the reactions occurring in the flare. This "disposable energy" will then be converted to luminous efficiency at various wavelengths. This model will allow a comparison not only of the effect of the disposable energy but also of any change in reaction temperature. For the purpose of comparing calculated and experimental values, all of the chosen oxidizers contain sodium. In order to make calculations and comparisons, it will be necessary to make various assumptions which will be presented at the appropriate time. The most basic assumption is that regardless of the system chosen, it will burn efficiently and to completion.

The thermodynamic calculations which form the basis for the determination of light yields were done using the NASA thermodynamics program.[4]

The results of these calculations are presented in Table I in terms of oxidizer to fuel ratio, O/F, adiabatic temperature, T_{AD}, the enthalpy at the adiabatic temperature, H_{AD}, and at 1200°K, H_{1200}, and the disposable energy, H_D. The optimum temperature is determined by varying fuel to oxidizer ratio until the maximum adiabatic temperature is reached. This ratio of fuel to oxidizer is then chosen as the formula. The formulas used all contain 5 percent binder in addition to the fuel and oxidizer. Using this composition, the enthalpy is calculated for a flame temperature of 1200°K which corresponds to the temperature at the boundary of the flare. The difference in these two enthalpies (H_{AD} - H_{1200}) is the disposable energy, H_D available for thermal excitation of atomic species. The disposable energy corresponds to the energy released when the system is burned to completion and the products allowed to cool to a temperature of 1200°K.

Computation of Light Output for Mg-$NaNO_3$ System

The disposable energy given in Table I can now be converted to luminous energy at a particular wavelength by converting the energies to radiant energy and then applying the luminous efficiency curve.[5] In order to calculate the maximum possible light output for each system in Table I, we make the following assumptions:

1. The optimum formula gives the maximum light.

2. There is no air augmentation of the flame, i.e., the only oxidizer is the nitrate or perchlorate.

3. No energy is lost except by radiation at the selected wavelength.

4. All the radiation is emitted at a specific wavelength, the maximum being λ - 555 nm, the peak of the eye response curve. This is valid if we assume that systems can be found which emit at specific wavelengths.

Sample Calculation

As an example, the calculation for Case 1, magnesium-sodium nitrate, is shown below. The radiant energy per gram of composition RE, is

$$RE = (1448.8 \text{ cal/g})(4.18 \text{ J/cal})(\text{sec/sec}) = 6.06 \times 10^3 \text{ (W-sec)/g}.$$

At the peak of the eye response, λ = 555 nm, the luminous efficiency is 680 lumens/watt. Therefore, converting radiant energy to luminous energy LE, gives

$$LE = [6.06 \times 10^3 \text{ (W-sec)/g}](680 \text{ lm/W}) = 4.12 \times 10^6 \text{ (lm-sec)/g}.$$

The luminous energy can now be converted to a measure of flare efficiency by dividing by 4π steradians. Assuming a point source emitting isotropically,

$$\text{Efficiency} = [4.12 \times 10^6 \text{ (lm-sec)/g}](1/4\pi) = 3.28 \times 10^5 \text{ (cd sec)/g}.$$

Thus, for the magnesium-sodium nitrate system, the maximum amount of light possible subject to the given assumptions is 3.28×10^5 (cd sec)/g (@ 555 nm).

In order to calculate the light output at 590 nm, we multiply the maximum light output by 0.757, the value of the eye response curve at 590 nm. Thus, at 590 nm, the maximum light output is

$$\begin{aligned} \text{Flare Efficiency} &= 3.28 \times 10^5 \text{ (cd sec)/g } (0.757) \\ &= 2.48 \times 10^5 \text{ (cd sec/g (@ 590 nm)}. \end{aligned}$$

The current magnesium-sodium nitrate flare typically gives a luminous efficiency of 50,000 (cd sec)/g. While this is light of all wavelengths, the majority of the light is in the vicinity of 590 nm. This means that, subject to the assumptions made, a five fold increase is all that is possible with the present magnesium-sodium nitrate system.

It is immediately evident that all the assumptions are incorrect to a certain extent. They were made so that there would be a common basis for comparison. To investigate the magnesium-sodium nitrate system in more detail, we will relax two of the four restrictions. Assuming still that the optimum formula is best and that all the light is emitted at 590 nm, we will relax the other restrictions. Figure 1 shows a plot of luminous efficiency as a function of the percent of disposable energy which goes into radiation. The plot is necessarily a straight line going through the origin.

If we now subtract energy losses from the disposable energy, the 5 times increase in light output becomes less. If, for example, we assume convection, conduction, and radiation losses in the infrared of 50 percent, the maximum percent disposable energy becomes half and the maximum light output is 1.24×10^5 (cd sec)/g. This is now only a 2.5 fold increase over the present composition. An even more realistic approximation for losses is 70 percent.[3] Using this figure gives a maximum light output of 74400 (cd sec)/g which is a 1.5 times increase in light output.

If we now permit air augmentation of burning, i.e., oxygen from the atmosphere mixing and aiding combustion, the available disposable energy per gram of solid increases by a factor of about 1.67. In addition to the increase from air augmentation, the disposable energy will increase by a factor of about 1.3 if the products are allowed to cool to 298°K. Making these two approximations, this now means that the maximum light output is 1.64×10^5 (cd sec)/g. Table II summarizes what has been concluded about the magnesium-sodium nitrate flare. These calculations seem to indicate that the largest realistic increase for magnesium-sodium nitrate flares is 2-3 times the present output.

Computation of Light Output for Other Systems

Table III summarizes the calculations of flare efficiencies at 555 nm and 590 nm for several illuminating flare formulas. The potential improvement factors are calculated assuming a present flare efficiency of 50,000 (cd sec)/g. This efficiency is for a fuel rich magnesium/sodium nitrate/binder formulation burning in air. Calculations and experiments show that a fuel rich magnesium-sodium nitrate flare burning in air has a total reaction energy of approximately 3200 cal/g. Taking the increased effect of air augmentation and product cooling into account increases the improvement potentials given in Table III by a factor of 2.2.

Other Potential Systems

There are probably other systems which are equally as effective as the sodium-containing systems. These, however, were beyond the scope of this paper since very detailed calculations would be required to compare these with the current systems. An example of another type system is magnesium burning in pure oxygen. This system obviously relies on emission from magnesium oxide which is a gas at the temperatures produced in the flame. Thermodynamic calculations show that the disposable energy in this system is 3277.1 cal/g. This corresponds to 5.60×10^5 (cd sec)/g at 590 nm or a 11 fold increase over the present magnesium-sodium nitrate system assuming no energy losses. The difficulty in comparing the two systems comes in not being able to satisfactorily evaluate the difference in the emission properties of atomic sodium and molecular magnesium oxide. Typically, the molecular species has a much lower oscillator strength than the atomic species and emits much less efficiently. Whether or not this is the case in this particular system is difficult to assess.

Another method of improving the light output of these systems would be to find a method of utilizing the disposable energy which is lost outside the visible wavelengths. This could be done by seeding the flames with other emitters which could be excited by this energy and emit light at wavelengths around 555 nm, the peak of the eye response curve. The increased temperatures of the other systems considered would aid in converting the lost disposable energy to the visible because of the increased population of the upper states of sodium due to the Boltzmann factor. For instance, the Boltzmann factor at the temperature of the aluminum/sodium nitrate flare is twice that of the magnesium/sodium nitrate flare which in itself could lead to a two-fold increase in efficiency.

Still another method would be the use of compositions which, when burned, give rise to species which then react to form excited molecular species and emit visible light. If these types of chemical reactions could be found, the spectra of the flares could be shaped to give more emission in the visible region of the spectrum.

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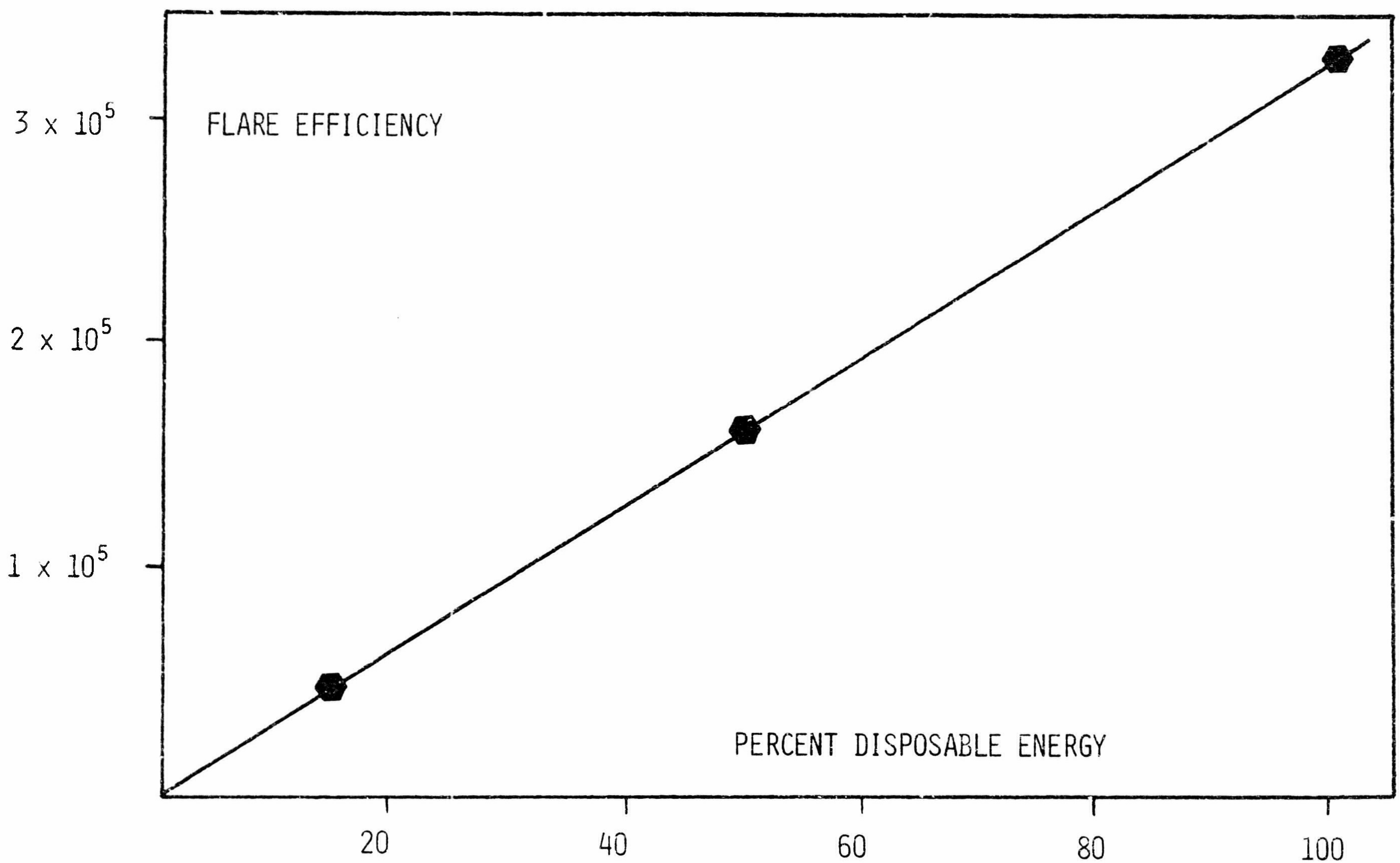
3 x 10^5
2 x 10^5
1 x 10^5
FLARE EFFICIENCY
PERCENT DISPOSABLE ENERGY
20
40
60
80
100

TABLE I

Computed Disposable Energy and other Thermodynamic Properties of Several Illuminating Flare Formulas

Case Number	System	O/F Ratio	T_{AD} (kelvin)	H_{AD} (cal/g)	H_{1200} (cal/g)	H_D (cal/g)
1	$Mg/NaNO_3$	1.4	3073	-754.2	-2203.0	1448.8
2	$Al/NaNO_3$	1.75	3371	-820.3	-2292.8	1472.5
3	$Be/NaNO_3$	3.50	3554	-996.6	-2974.5	1977.9
4	$Si/NaNO_3$	2.54	2855	-921.5	-2018.0	1096.6
5	$Mg/NaClO_4$	1.50	3156	-452.8	-2534.6	2081.8
6	$Al/NaClO_4$	1.80	3594	-483.2	-2795.8	2312.6
7	$Be/NaClO_4$	3.60	3736	-582.4	-3553.0	2970.6
8	$Si/NaClO_4$	2.60	2998	-539.5	-2469.8	1930.3
9	Mg/O_2	0.80	3283	-26.9	-3304.0	3277.1

Notes:

O/F is oxidant to fuel ratio.
T_{AD} is computed adiabatic temperature in degrees Kelvin.
H_{AD} is computed enthalpy of the combustion products at T_{AD}.
H_{1200} is computed enthalpy of the combustion products at 1200°K.
H_D, called disposable energy, is equal to $H_{AD} - H_{1200}$.

TABLE II

Summary of Maximum Flare Efficiency Predicted for the Mg-$NaNO_3$ System

	Mg/$NaNO_3$	Mg/$NaNO_3$/Air& Cooling
Disposable Energy	1448 cal/g	3186 cal/g
Maximum Flare Efficiency: Assumes 100% of disposable energy is converted to 555 nm photons.	3.28×10^5(cd sec)/g	7.21×10^5(cd sec)/g
Maximum Flare Efficiency: Assumes 100% of disposable energy is converted to 590 nm photons.	2.48×10^5(cd sec)/g	5.46×10^5(cd sec)/g
Maximum Flare Efficiency: Assumes 30% disposable energy is converted to 590 nm photons.	7.45×10^4(cd sec)/g	1.64×10^5(cd sec)/g
Potential Improvement Factor: (computed/current typical value for Mg-$NaNO_3$ Flare).	1.5	3.3

Notes:

The values in the last column include a 1.67 fold increase for air augmentation and a 1.3 fold increase for the added energy released as the species cool from 1200°K to 298°K. The composite of the above two factors is 2.2 fold increase.

TABLE III

Computed Flare Efficiency at 555 nm and 590 nm of Several Illuminating Flare Formulas

Case Number	System	H_D (cal/g)	Efficiency at 555 nm (cd sec/g)	Efficiency at 590 nm (cd sec/g)	Potential Improvement Factor
1	$Mg/NaNO_3$	1448.8	3.28×10^5	2.48×10^5	5.0
2	$Al/NaNO_3$	1472.5	3.33×10^5	2.52×10^5	5.1
3	$Be/NaNO_3$	1977.9	4.47×10^5	3.39×10^5	6.8
4	$Si/NaNO_3$	1096.5	2.48×10^5	1.88×10^5	3.8
5	$Mg/NaClO_4$	2081.8	4.71×10^5	3.56×10^5	7.1
6	$Al/NaClO_4$	2312.6	5.23×10^5	3.96×10^5	7.9
7	$Be/NaClO_4$	2970.6	6.72×10^5	5.1×10^5	10.2
8	$Si/NaClO_4$	1930.3	4.37×10^5	3.29×10^5	6.6
9	Mg/O_2	3277.1	7.41×10^5	5.61×10^5	11.1

Notes:

H_D, called disposable energy, is equal to $H_{AD} - H_{1200}$.

The efficiency values are a measure of the flare's light output over time and per gram of flare composition. These values result from the assumption that all the disposable energy is converted to photons of wavelengths 555 nm or 590 nm as noted.

The potential improvement factor is the ratio of the listed flare efficiency and the current typical efficiency value of a $Mg-NaNO_3$ flare. The improvement factor is about 2.2 fold larger if one assumes that air augmentation and cooling typical of case 1 is applicable to all cases.